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Preliminary Investigation of the Fabrication and Properties of Hafnium Carbide

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Abstract

In spite of the 7030° F melting point for HfC reported in 1930, and therefore the obvious potential of the material for very high temperature application, practically no information on its physical and mechanical properties is known. The Lewis Research Center and other research groups have recently initiated studies on this material. This paper will present the results of fabrication studies, room temperature evaluations of bend strength, elastic modulus, and microhardness, and elevated-temperature evaluations of bend strength thermal expansion, thermal conductivity, specific heat and electrical resistivity.

Introduction

In the search for materials to fill today's and tomorrow's high temperature requirements for a variety of applications, refractory inorganic compounds command attention because of their very high melting points. Many of the carbides, borides, and nitrides of the transition metals in groups IVA, VA, and VIA of the periodic table have melting points well above 5000° F, the highest melting point of any metal or simple compound being that for the carbide of the metal hafnium.

In 1930, Agte and Alterthum¹ prepared hafnium carbide from hafnium dioxide and lampblack and determined the melting point of the hafnium carbide to be $7030 \pm 270^\circ \text{F}$ —the value that is accepted today. The following year, 1931, Agte and Moers² prepared hafnium carbide in wire form by the reaction of hafnium tetrachloride with a hydrocarbon gas at an incandescent tungsten filament. The wire was

then used for the measurement of electrical resistivity. A room temperature value of 42.9×10^{-6} ohm-in. was determined, which was until recently the accepted value. Also, in 1931, Agte³ did x-ray diffraction work on hafnium carbide and determined a lattice parameter value of 4.69 Å for the carbide sodium chloride type of structure.

After these initial investigations, practically no work was done on hafnium carbide until limited quantities of high-purity hafnium metal and hafnium dioxide became available in the United States following the perfection of a solvent extraction method for the separation of hafnium from zirconium by the U. S. Bureau of Mines in 1952. In 1953 and 1954 various research groups prepared hafnium carbide by hot pressing mixtures of high-purity hafnium dioxide and carbon or high-purity hafnium metal and carbon.⁴⁻⁶ The carbides produced were examined by x-ray diffraction analyses, and microhardness measurements were made. Cotter and Kohn⁵ plotted the lattice parameter against the combined carbon content of several carbides produced, and by extrapolation found a value of 4.641 ± 0.001 Å for the stoichiometric carbide. Their microhardness measurements were made with a Knoop indenter under a 100-g load, and a value of approximately 2600 was obtained—a hardness in the silicon carbide range.

The next show of interest in hafnium carbide began in 1959 when scientists at Metallwerk Plansee AG, Reutte/Tirol, Austria prepared hafnium carbide for use in the study of binary carbide systems, and for use as a substitute for titanium carbide and tantalum carbide in the standard cutting tool compositions.^{7,8} Their continued investigations in 1960 resulted in the determination of the homogeneity range and the room temperature electrical resistivity of hafnium carbide. Benesovsky and Rudy⁹ found the homogeneity range of hafnium carbide at 2800° F to extend from 37 atomic-% carbon and a corresponding lattice constant of 4.614 Å to 50 atomic-% carbon and a corresponding lattice constant of 4.631 Å. Rudy and Benesovsky¹⁰ measured the electrical resistivity at room temperature and found it to be 14.6×10^{-6} ohm-in. This is only 6% higher than the resistivity of hafnium metal, 13.8×10^{-6} ohm-in., and about one-half that of stainless steel. (The resistivity of copper is 0.66×10^{-6} ohm-in.)

Considerable work was done on hafnium carbide in the United States in 1960. Investigations were made on hafnium carbide which involved the plasma spraying and arc melting of the carbide.^{11,12}

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Engelke and co-workers¹¹ ran oxidation tests on arc-melted hafnium carbide buttons, and on other high melting point carbides. Hafnium carbide alone and in combination with tantalum carbide compared favorably with titanium carbide, which is the most oxidation resistant of the very high melting point carbides. It was noted that the mixed carbide oxidized to form a glassy coating which acted as an effective barrier against oxidation at 2190° F.

Physical property measurements on hafnium carbide were also performed in 1960. Heat capacity, thermal expansion, thermal conductivity, and electrical resistivity determinations were made. The results of these investigations will be given in one of the following sections.

Lewis Research Center began its studies of hafnium carbide in 1957. Investigations of the compatibility of uranium dioxide and uranium carbide with hafnium carbide and several other high melting materials in the temperature range of 3500–5000° F were undertaken to indicate combinations that may be suitable for a dispersion-type fuel element for a nuclear reactor.^{13,14} It was found that hafnium carbide did not react with uranium dioxide up to 5000° F and that no reaction occurred between hafnium carbide and uranium carbide at 4600° F.

Current Research

Fabrication of High-Density Hafnium Carbide Bodies

Following the compatibility studies, an investigation of fabrication techniques for the production of high-density hafnium carbide bodies was begun. The first fabrication technique tried was the conventional cold press-sinter process. Hafnium carbide powder of 3.1 μ average particle size was used to produce $\frac{1}{2}$ in. diam pellets about $\frac{1}{4}$ in. thick. Additions of wax binder up to 4% were tried, and die pressures in the 20,000–60,000 psi range were employed. Pellets were also produced by hydrostatically pressing both loose and pre-compacted hafnium carbide powders to which wax or 10% cobalt “fugitive binder” had been added. The cobalt not only acts as a green binder but during sintering promotes densification by diffusion before being volatilized out of the compact. A constant hydrostatic pressure of 50,000 psi was employed. The pellets contain-

ing wax were sintered for 30 min at 5000° F under a static argon atmosphere of 40 mm Hg pressure. The pellets containing cobalt binder were sintered for 1 hr at 4400° F in a vacuum of 2×10^{-4} mm Hg pressure. The highest densities obtained for each technique are presented in Table I.

TABLE I
Densities of Hafnium Carbide Pellets

Process	Binder	Binder, wt-%	Pressure, psi		Sintering conditions			Theoret. density, %
			Cold press	Hydro-static	Temp., ° F	Time, min	Atm	
Cold press	Wax	2	40,000	—	5000	30	40 mm Ar	71
Hydrostatic press	None	—	—	50,000	5000	30	40 mm Ar	78
Cold press and hydrostatic press	Wax	2	30,000	50,000	5000	30	40 mm Ar	94
Hydrostatic press	Cobalt	10	—	50,000	4400	60	2×10^{-4} mm Hg vac	95

From the results in Table I it can be seen that high-density binderless hafnium carbide bodies were produced only when employing two-step pressing procedures and a very high sintering temperature or when using a volatile metal binder.

The third fabrication technique tried was hot pressing. This was accomplished in graphite dies heated by an inductively heated graphite sleeve susceptor. The bodies produced were about $\frac{5}{8}$ in. in diameter and $\frac{1}{4}$ in. thick. Following some preliminary hot pressing trials to establish the ranges of investigation for the three hot pressing variables, the effect of each variable, temperature, pressure, and time was determined over its range while the other two variables were held constant.¹⁵ The effect of each variable on the density is shown graphically in Figure 1, and the table included with the figure gives the ranges of investigation for the variables. Densities of 99% of theoretical were achieved when hafnium carbide was hot pressed at about 4200° F for 15 min under a pressure of about 4000 psi. Density can be seen to be greatly dependent upon hot pressing temperature in the 3500 to 4000° F temperature range, while the effects of time

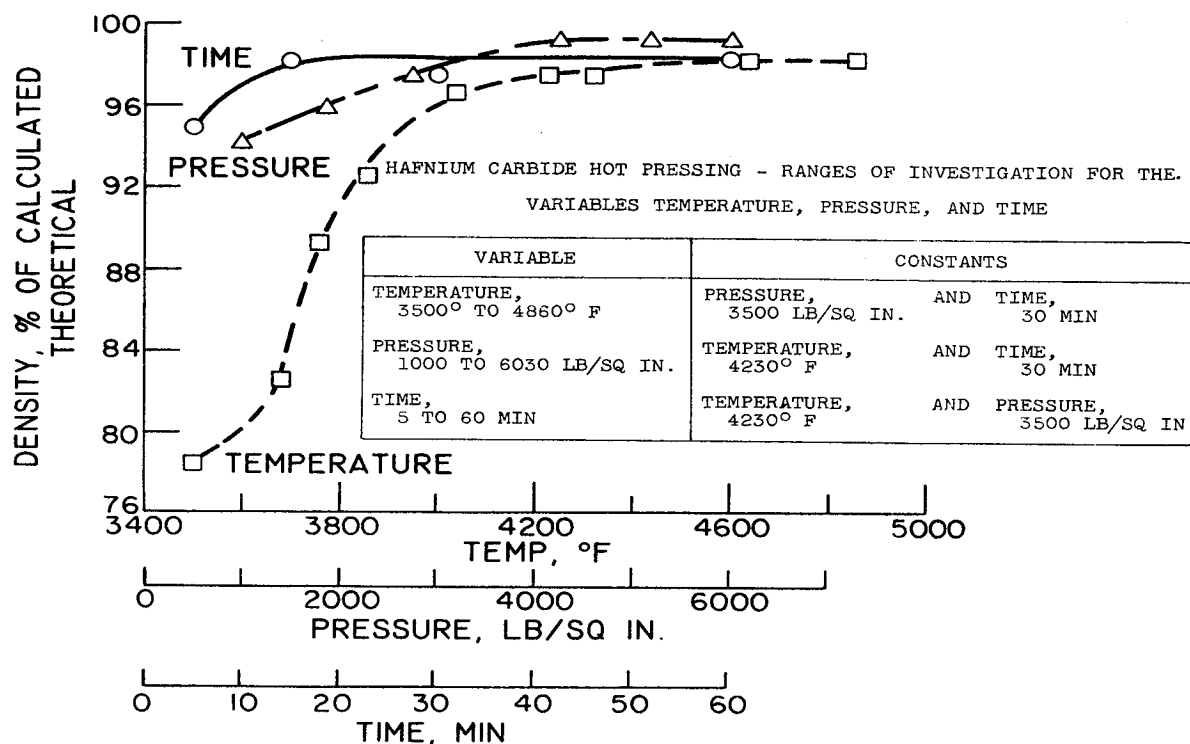


Fig. 1. Variation of density with hot pressing temperature, pressure, and time.

and pressure are seen to be much less significant. No further increases in density are realized for hot pressing times of over 15 min and for pressures above about 4000 psi.

Mechanical Properties

Based upon the results of the fabrication studies, hafnium carbide bars 4 in. long with cross sections $\frac{1}{4}$ by $\frac{1}{2}$ in. were produced by hot pressing. The hot pressing conditions were: temperature, 4700° F; pressure, 2500 psi; and time, 15 min. Two lots of hafnium carbide powder were used, the original lot, lot A of 3.1 μ average particle size and a new lot, lot B, of 1.3 μ average particle size. The lot B bars produced were each cut into six transverse rupture test bars 2 in. long with cross sections of 0.12 by 0.25 in. Bars of these dimensions were also formed from hydrostatically pressed and sintered cylinders of lot B powder. These cylinders were produced by hydrostatically pressing at 50,000 psi hafnium carbide powder to which 10% fugitive cobalt binder had been added. The green compacts were then sintered

at 4400° F for 1 hr in a vacuum of 2×10^{-4} mm Hg pressure. All test bars were surface ground to a finish of about 25 μ in. The test bar density range was 93 to 96% of theoretical density for both the hot-pressed bars and the sintered bars.

The test bars were tested in an Instron tensile testing machine equipped with a compression load cell. The four-point loading method was employed, which subjects an extended area of the test bar to a constant bending stress. The movable crosshead of the testing machine had a travel rate of 0.002 ipm, which resulted in a loading rate of 20,000 psi/min on the outer fibers of the tension face of the test bar. Load-strain data were obtained in some cases by use of wire resistance strain gages bonded to the tension and/or compression faces of the test bars.

The modulus of rupture (outer fiber tensile stress at fracture) was determined by the beam formula,

$$\sigma = \frac{3Pl}{bd^2}$$

where σ is the stress, psi; P is the load, lb; l is the common side support edge-load edge spacing, in.; b is the bar breadth, in.; and d is the bar thickness, in.

The modulus of elasticity was determined by the slope of stress-strain curves which were plotted from stress-strain data computed from load-strain gage readings taken during incremental loading of the test bars.

Metallographic examination of fracture sections of hot-pressed and sintered bars of about the same density indicated that there was considerable difference in grain size, with the sintered bar having grains over three times as large as those of the hot-pressed specimen. The large grains are due to the liquid cobalt binder, which promotes denser packing of the mobile carbide particles by its surface tension and a subsequent high degree of coalescence of neighboring grains. Table II presents the results of the transverse rupture strength and microhardness determinations.

The figures in Table II indicate that the hot-pressed bars are considerably stronger than the sintered specimens. This difference can be attributed to the marked difference in grain size. The elastic modulus was found to be the same for both the sintered and hot-pressed bars.

The open literature does not reveal any transverse rupture strength

TABLE II
Hafnium Carbide (Lot B) Transverse Rupture Strength,
Modulus of Elasticity, Knoop Microhardness, and Grain Size

	Hot pressed	Sintered
Modulus of rupture, psi	31,000	24,000
Modulus of elasticity, psi	46.5×10^6	46.5×10^6
Knoop microhardness, kg/sq mm (50 g load)	2063	2042
Average grain diam, μ	12.7	42.4

data for binderless sintered or hot-pressed hafnium carbide. However, some work on zirconium carbide has been done, and a great deal of work has been done on titanium carbide, which is well known for its good strength and oxidation resistance. The three metals titanium, zirconium, and hafnium are members of the IVA subgroup in the periodic table.

Table III gives some transverse rupture strength values for zirconium carbide and titanium carbide.

TABLE III
Transverse Rupture Strength for Binderless Carbides, psi

	psi	Test-bar theoret. density, %
Hafnium carbide (lot B)	31,000	91-96
Zirconium carbide (ref. 16) ^a	30,000	95-100
Titanium carbide (ref. 17) ^b	57,000	95
	92,000	99.8

^aEighty per cent of powder $< 2 \mu$.

^b- 325 mesh.

The transverse rupture strength of hafnium carbide is seen to be slightly higher than for zirconium carbide, but it is considerably less than for titanium carbide. The effect of density on strength is very great in the case of titanium carbide above 95%. As seen from Table III an over 60% increase in strength results when the density of titanium carbide is increased from 95 to 99.8%. It is likely that significant increases in the strength of hafnium carbide bodies will also be obtained when higher density bodies are made.

Some work has been done on hafnium carbide with 10% cobalt binder.⁸ This work was done as part of an investigation of experi-

mental cutting-tool compositions. Nine different carbides including hafnium carbide, each with 10% cobalt binder, were tested for transverse rupture strength. Hafnium carbide ranked third in strength behind tungsten carbide and columbium carbide, but surpassed its sister carbides titanium carbide and zirconium carbide. This would indicate that hafnium carbide may very well be stronger than these two carbides in binderless bodies when better fabrication techniques are developed.

Room- and elevated-temperature transverse rupture strengths were also determined at Lewis Research Center on the 4-in. hot-pressed hafnium carbide bars produced from lot A powder. The density range for these test bars was 95 to 97% of theoretical density. The tests were conducted at room temperature and at 1600, 2000, and 2400° F in an argon atmosphere. The nominal cross section of these bars was $\frac{1}{2}$ by $\frac{1}{4}$ in. They were tested in a commercial Globar resistor furnace into which a lever-loading system and a protective atmosphere chamber had been incorporated. The test bars were supported on silicon carbide knife edges over a 3-in. span, and loading was by a single silicon carbide knife edge at the center of the 3-in. span. The loading rate was 7500 psi/min on the outer fibers of the tension face at the midpoint of the bar test span.

Metallographic examination of one of the lot A hafnium carbide test bars showed that the test temperature had no effect on structure after test at 2400° F. The average grain diameter of this bar was 29.8 μ , which is over twice as great as that of the lot B bar produced under the same hot press conditions. This can be attributed to the finer initial particle size of the lot B powder.

Table IV presents the results of the room- and elevated-temperature strength determinations on lot A hafnium carbide, and some literature values on zirconium carbide and titanium carbide.

The strength of hafnium carbide like titanium carbide decreases with increasing test temperature. At room temperature, the strength of the hafnium carbide is only 27% that of the titanium carbide, and at 2000° F only 42% that of the latter. The higher strengths of the titanium carbide bars may be due in part to the fact that they were 100% dense while the hafnium carbide bars had a porosity of 3 to 5%. Zirconium carbide, however, although having a room temperature strength a little less than hafnium carbide, maintains its strength at least to 2900° F; and, in fact, at the intermediate temperature of

TABLE IV
Elevated-Temperature Transverse Rupture
Strength of Binderless Carbides, psi

	Test temperature, ° F					
	Room	1600	2000	2200	2400	2900
Hafnium carbide (lot A)	34,100	33,300	25,200	—	15,800	—
Zirconium carbide (ref. 16)	30,000 ^a	—	47,600 ^b	—	—	31,700 ^c
Titanium carbide (ref. 17) ^d	124,000	95,000	60,000	25,000	—	—

^aAverage for four test bars with theoretical densities 95% or over (80% of powder under 2 μ).

^bAverage for two bars with theoretical densities of 96 and 97% (80% of powder under 2 μ).

^cAverage for two bars with theoretical densities of 96 and 99% (80% of powder under 2 μ).

^dTest bars hot pressed from 2 to 8 μ powder; bars are 100% dense.

2000° F, it exhibits a strength over 50% greater than that at room temperature. The zirconium carbide test bars tested at the elevated temperatures had densities varying from 96 to 99% of the theoretical density, and were made from powder of which 80% of the particles was under 2 μ diam. Perhaps higher density bodies produced from finer hafnium carbide powders will permit the attainment of higher room temperature strengths and retention of elevated-temperature strength.

The Knoop microhardness for a representative lot A hafnium carbide bar was 2505 kg/mm². This is a considerably higher hardness than that of the lot B bars, which had Knoop microhardness of only 2063. Coinciding with the higher hardness for the lot A bars is a higher room temperature transverse rupture strength. This is contrary to what would be expected, since higher strengths would be expected for the lot B test bars, which had a grain size less than one-half that of the lot A test bars. Since the two types of bars were in about the same density range, the differences in hardness and strength are attributed to differences in chemical composition. Table V gives the chemical and x-ray analyses for the hafnium carbide powder lots A and B.

Lot A contains more metal impurities than lot B, but considerably less free carbon than lot B and no oxygen and nitrogen. These differences are probably responsible for the differences in the properties of the bars produced from the two lots.

TABLE V
Chemical and X-ray Analyses of Hafnium
Carbide Powder, Lots A and B

Lot No.	Hf:C ratio	Chemical analyses, weight per cent								Lattice parameter, A
		Carbon Com- bined	Free	Hf	Zr	Ti	B	O	N	
Theoret.	14.9	6.3	—	93.7	—	—	—	—	—	4.641
A	14.9	6	0.03	89.4	3.45	0.39	0.72	—	—	4.631
B	15.1	6.05	0.30	91.2	1.40	0.50	—	0.45	0.10	4.638

Physical Properties

Electrical resistivity, thermal conductivity, and specific heat over a range of temperature in vacuum were determined for hafnium carbide bar produced from lot A hafnium carbide powder. A hot-pressed bar, 4 by $\frac{1}{2}$ by $\frac{1}{4}$ in. and 96.2% theoretical density was diamond wheel ground on all sides to remove possible surface contamination, and the cross section of the bar was reduced to 0.20 by 0.023 in. This cross section gave an electrical resistance sufficient to permit resistance heating of the bar to a temperature of 4600° F with the available power supply. The measurements were made by Pike with apparatus at the Union Carbide Corp.¹⁸

Figure 2 shows the variation with temperature of the electrical resistivity of hafnium carbide. Two resistivity curves are shown, the lower curve for the first series of measurements, and the upper curve

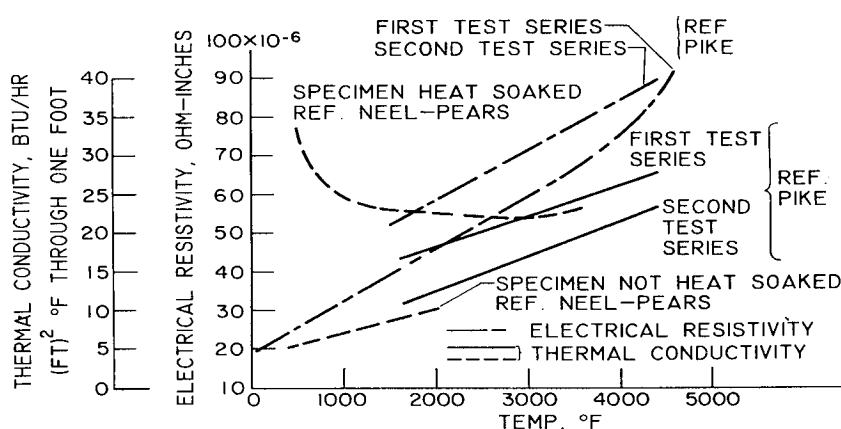


Fig. 2. Variation of the electrical resistivity and thermal conductivity of hafnium carbide with temperature.

for a second series of measurements. The nonlinearity of the portion of the lower curve above 3200° F and the displacement of the curves for the first and second series of measurements are ascribed as being due to sample evaporation occurring in the first series of tests. This would then result in a material whose physical properties were different from the starting material. A deposit on the windows of the vacuum test chamber was examined by x-ray fluorescence and found to contain hafnium; the presence of carbon could not be determined by the method employed. It is postulated that residual oxygen gas in the furnace reacted with the carbide forming hafnium dioxide which was then thermally removed at temperatures of 3500° F and above.

Figure 2 also shows the variation with temperature of the thermal conductivity of hafnium carbide. Four thermal conductivity curves are shown; two are for the lot A hafnium carbide bar, and for comparison two are for hafnium carbide specimens tested by Neel and Pears.¹⁹ The two curves for the lot A bar again exhibit the apparent change in the material upon repetition of a series of tests. An appreciably lower thermal conductivity resulted when a second series of measurements were made, as can be seen by the downward displacement of the solid curve for the second series with respect to the solid curve for the first series. The thermal conductivity measurements by Neel and Pears are represented by the two dotted curves. The upper dotted curve is for a specimen which was heat soaked before testing at 4500° F for 15 min. The lower specimen was tested in the as-received condition. Tests were terminated in both cases when the specimens cracked. This occurred at about 3600° F for the heat-soaked specimen and at about 2000° F for the unannealed specimen. As can be seen, the curves are widely separated, and in addition their trends with temperature are markedly different. It might be expected that the thermal conductivity curve for the heat-soaked specimen would fall close to the curve resulting from the second series of measurements on the Lewis bar, since both had received a heat treatment. This was not the case, however; and, in fact, the reverse was true. The higher temperature portion of the Neel-Pears heat-soaked specimen curve is closer to the curve for the first series of measurements on the lot A bar, while the curve for the unannealed Neel-Pears specimen has values approaching the level of the second series data on the lot A bar.

Figure 3 shows the variation of specific heat with temperature for the lot A hafnium carbide bar and for a hafnium carbide specimen tested by Neel and Pears.¹⁹ The dotted upper curve for the Lewis bar is limited, but it establishes a level higher than that indicated by the dotted curve for the Neel-Pears specimen. The specific heat for the latter rises sharply with increasing temperature to about 2000° F, and then drops slightly with further temperature rise to 5000° F. A transient method was used to determine the specific heat of the Lewis bar, while an ice chamber-drop test procedure was employed for measurement of the specific heat of the Neel-Pears specimen.

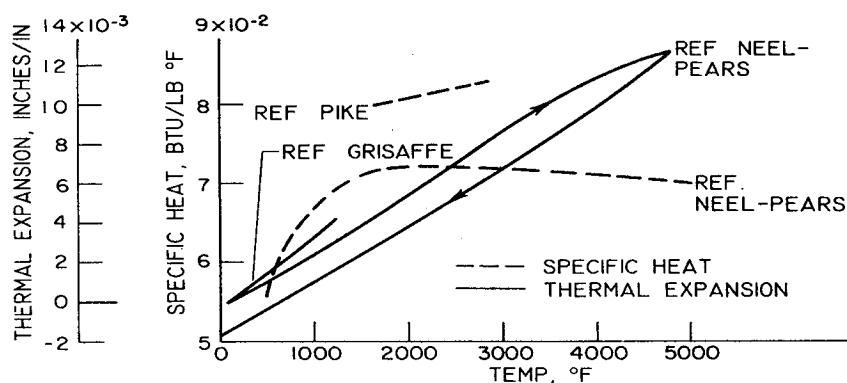


Fig. 3. Variation of the specific heat and thermal expansion of hafnium carbide with temperature.

Grisaffe, at Lewis Research Center, determined the thermal expansion of lot A hafnium carbide bodies from room temperature to 1200° F.²⁰ Figure 3 shows the variation of thermal expansion with temperature for the Lewis specimens (solid curve) and for a specimen (solid curves) measured by Neel and Pears.¹⁹ The latter underwent a small permanent reduction in length as indicated by the nonconcurrency of the heating and cooling curves, while the Lewis specimen curves were coincident for heating and cooling. The thermal expansion of hafnium carbide appears to be approximately linear up to 4000° F. The nonconcurrency of the heating and cooling curves for the very high temperature measurements of Neel and Pears may be due to densification shrinkage.

Inspection of the curves of physical property data shown indicates that the data of different investigators are not in very good agree-

ment. Not only are the relative magnitudes of the various parameters different but also the trends with temperature are contradictory. The experimental techniques employed seem sound since the investigators have run standard material in their apparatus and achieved good checks with literature values. This state of affairs points to a need for a complete characterization of the hafnium carbide material tested. Whether the irreversible changes noted for the electrical resistivity, thermal conductivity, and thermal expansion of hafnium carbide are due to impurities or to physical changes in the specimen brought about by test itself is not known. Specimen thermal history (fabrication and heat treatment) may be of considerable importance in determining how a material will perform under test. This aspect is discussed by Neel and Pears²¹ who describe peculiarities in the thermal expansion of a number of refractory materials including hafnium carbide.

Summary

Hafnium carbide is one of the highest melting point materials known, and thus ultimately may be of interest for high temperature applications such as rocket nozzles, re-entry structures, and reactor fuel elements. It has been the purpose of the research described herein to attempt to learn how to make solid dense bodies of this material and then to characterize its mechanical and physical properties.

It has been found that hot pressing at temperatures of the order of 4200 to 4800° F can produce bodies of densities of 98 to 99% of theoretical. Some cold press-sinter techniques were found that produce bodies of densities of about 95% of theoretical.

The electrical resistivity, specific heat, and thermal expansion of hafnium carbide were found to be similar to values reported for other carbides and about one-half the values for the austenitic stainless steels. Like that of the metals, the electrical resistivity of hafnium carbide increases with increasing temperature. The thermal conductivity of hafnium carbide was found to be about the same as that of the austenitic steels.

Strength data up to 2400° F on both hot-pressed and cold-pressed and sintered hafnium carbide bars have not been encouraging. Strength decreases with increase in test temperature and at 2400° F

is appreciably less than the strengths of the carbides of zirconium, titanium, and silicon. It is suggested that higher density, finer grained bodies than tested herein may greatly increase strength, particularly at low temperatures.

The microhardness of hafnium carbide is high, and is comparable to that of silicon carbide. The room temperature modulus of elasticity is about 46,000,000 psi and hafnium carbide remains brittle at least to a temperature of 2400° F, which was the highest test temperature so far employed.

The properties described herein generally characterize the material, but the investigation has emphasized the importance of raw material and processing variables on the properties, particularly strength and hardness, of this material. Lack of large quantities of consistent, high-purity raw material has caused inconsistencies in the data. Material has been available to date only in small lots with quality improving somewhat with later dates of procurement. It is clear that anyone who considers data on properties of these materials must be alert to the importance of raw materials and fabrication techniques used to provide the test specimens.

References

1. Agte, C., and H. Alterthum, "Systems of High-Melting Carbides; Contributions to the Problem of Carbon Fusion," *Z. Tech. Physik*, **11**, 182 (1930).
2. Agte, C., and K. Moers, "Methods for the Preparation of Pure High-Melting Carbides, Nitrides, and Borides and a Description of a Few of Their Properties," *Z. anorg. u. allgem. Chem.*, **198**, 233 (1931).
3. Agte, C., "X-ray Diffraction Analyses on High-Melting Carbides, Nitrides and Borides," Dissertation Techn. Hochschule Berlin, 1931.
4. Glaser, F. W., D. Moskowitz, and B. Post, "A Study of Some Binary Hafnium Compounds," *Trans. AIME*, **197**, 1119 (1953).
5. Cotter, P. G., and J. A. Kohn, "Industrial Diamond Substitutes: I—Physical and X-ray Study of Hafnium Carbide," *J. Am. Ceram. Soc.*, **37**, 415 (1954).
6. Curtis, C. E., L. M. Doney, and J. R. Johnson, "Some Properties of Hafnium Oxide, Hafnium Silicate, Calcium Hafnate, and Hafnium Carbide," *J. Am. Ceram. Soc.*, **37**, 458 (1954).
7. Nowotny, H., F. Benesovsky, and R. Kieffer, "Hafnium Carbide and Its Behavior Towards Other Carbides of the High Melting Point Transition Metals," *Planseeber. Pulvermetal.* **7**, 79 (1959).
8. Kieffer, R., F. Benesovsky, and K. Messmer, "Hafnium Carbide Containing Hard Metals," *Metall*, **13**, 919 (1959).
9. Benesovsky, F., and E. Rudy, "Contributions to the Construction of the Systems Zirconium-Carbon and Hafnium-Carbon," *Planseeber. Pulvermetal.*, **8**, 66 (1960).

10. Rudy, E., and F. Benesovsky, "On the Electrical Conductivity of the Very High Melting Point Carbides and Carbide Mixed Crystals," *Planseeber. Pulvermetal.*, **8**, 72 (1960).
11. Engelke, J. L., F. A. Halden, and E. P. Farley, "Synthesis of New High Temperature Materials," WACD TR 59-654, 1960.
12. Eisenlohr, A., "Properties of Plasma Sprayed Materials," AF Contract 33(616)6376, 1960.
13. Gangler, J. J., W. A. Sanders, and I. L. Drell, "Uranium Dioxide Compatibility with Refractory Metals, Carbides, Borides, Nitrides, and Oxides Between 3500° and 5000° F," NASA TN D-262, 1960.
14. Creagh, J. R. W., "NASA Research Program on Compatibility of Uranium Monocarbide," TID 7589, 30, 1960.
15. Sanders, W. A., and S. J. Grisaffe, "The Hot-Pressing of Hafnium Carbide (Melting Point, 7030° F)," NASA TN D-303, 1960.
16. Hall, A. R., and W. Watt, "The Bend Strength of Sintered Zirconium Carbide," Royal Aircraft Establishment T. N. No. 137, 1960.
17. Glaser, F. W., and W. Ivanick, "Sintered Titanium Carbide," *Trans. AIME*, **194**, 387 (1952).
18. Pike, J. N., "Research in Physical and Chemical Principles Affecting High Temperature Materials for Rocket Nozzles," Union Carbide Research Institute, Semiannual Progress Rept., 1960.
19. Neel, D. S., and C. D. Pears, "The Thermal Properties of Thirteen Solid Materials to 5000° F or Their Destruction Temperatures," A. F. Contract 33(616)-6312 (1960).
20. Grisaffe, S. J., "Thermal Expansion of Hafnium Carbide," *J. Am. Ceram. Soc.*, **43**, 494 (1960).
21. Neel, D. S., and C. D. Pears, "The Strange Thermal Motions of Some Refractory Materials at Temperatures Up to 5000° F," Southern Research Institute Bull. Jan. 1961.